

Models for predicting the surface tension of biodiesel and methyl esters

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ABSTRACT

Biodiesel is obtained from vegetable oils or animal fats, and it is emerging as an attractive alternative to petroleum diesel.

The surface tension of biodiesel has been little studied, although it plays an important role in the atomization process.

In this work, models of group contribution, corresponding state, and empirics were tested to predict the surface tension of methyl esters, whereas two mixing rules were used to estimate the surface tension of biodiesel as a function of its chemical composition and temperature. A statistical analysis (by means of the relative error (D), standard deviation (SD), correlation coefficient (R^2), analysis of variance (ANOVA), and parity plots) was applied to evaluate the predictive capability of models.

The empirical correlation developed to estimate the surface tension of fatty acid methyl esters (FAMEs) closely reproduces the experimental data, with an average absolute deviation (AAD) of 0.93%. This model highlights the dependence between the surface tension with its molecular weight and temperature.

On the other hand, the simple mixing rule on mass fraction basis offers the best prediction for the biodiesel surface tension ($AAD=2.88\%$).

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Nomenclature

mN	milli-Newton = 1×10^{-3} N
mJ	milli-Joule = 1×10^{-3} J
FAME	Fatty Acid Methyl Ester
T	Temperature, K
M	Molecular Weight, g/mol
N	Number of Double Bonds in the Fatty Acid Chain
n_{exp}	Number of Experimental Points
ANOVA	Analysis of Variance
DF	Degrees of Freedom
ρ	Density, g/cm ³
AAD	Average Absolute Deviation, %
D	Deviation or Relative Error, %
x_i	Mole Fraction of the i th FAME
w_i	Mass Fraction of the i th FAME
SD	Standard Deviation

1. Introduction

Renewable bio-fuels have been gaining momentum in recent years due to environmental, economic, and geopolitical considerations, including: global warming, rising crude oil prices, and depletion of petroleum reserves [1,2]. A bio-fuel that is being studied with great interest by the scientific community is biodiesel, a mixture of alkyl esters of long chain fatty acids derived from lipid raw material [1,3,4], where the trans-esterification reaction is the most common method to produce biodiesel [1,2]. The interest for biodiesel lies in the fact that can be considered as an alternative or complement for the fossil diesel, which means that it can be used in its neat form or blended with fossil diesel inside of compression ignition engines [1].

Biodiesel has various advantages in comparison to the fossil diesel that includes: (1) it is a source of renewable energy [1,2], (2) it can help to reduce the CO₂ emissions to the atmosphere [1], (3) practically, it not contains sulfur, helping to reduce the acid

rain, (4) it is biodegradable and non-toxic [1,3], that is very convenient in case of accidental spills, (5) it has excellent lubricity, helping for the longer life of engines [2], and (6) it has higher flashpoint, contributing to industrial safety, because the storage and transportation conditions are facilitated [2]. Currently, the higher cost is the main disadvantage of biodiesel, making it less competitive than diesel. In addition, biodiesel, in comparison with fossil diesel, has the following drawbacks: (1) less calorific value, causing an increment on fuel consumption, as well as a reduction of the engine power, (2) lower oxidation stability, reducing its storage life, and (3) higher cloud point and pour point, making it difficult to use at low temperatures [2].

To understand the qualities and potential of biodiesel, it is necessary to know in depth its chemical and physical properties. One physical property that plays an important role in the atomization process is the surface tension [1], because higher surface tension makes the drop formation difficult, leading to an

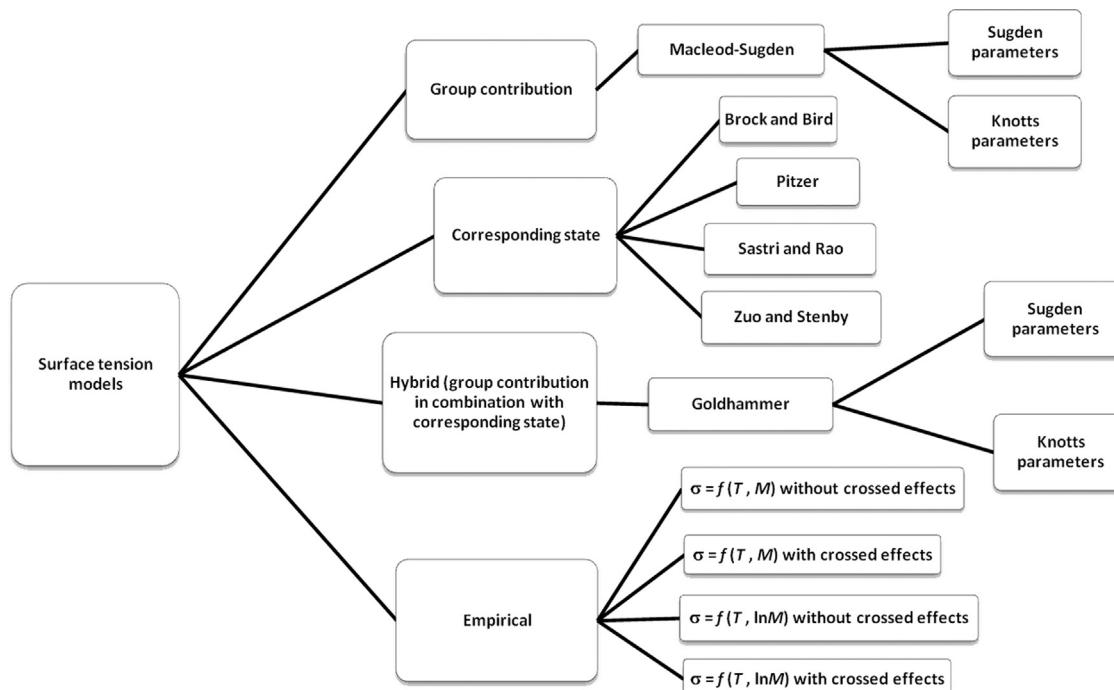


Fig. 1. Models tested in this work.

inefficient fuel atomization [5]. Surface tension is defined as the force exerted in the plane of the surface per unit length, and it is a physical property of fluids that occurs by intermolecular forces near the surface. Surface tension also reveals information on the structure of the surface region and it has a great influence on the interface mass transfer. For the above reason, the surface tension is important for the development, design and simulation of some industrial processes, as well as chemical engineering, oil recovery and environmental protection [6,7].

The surface tension of biodiesel varies depending on the raw material used to produce it (vegetable oils or animal fat), mainly due to the distribution of fatty acids in triglycerides. Additionally, the surface tension is a function of temperature. Experimental surface tension data for biodiesel over a wide range of composition and temperature are scarce and their measurements tend to be expensive and time-consuming. For the above reason, methods of estimation are required [4].

This work focuses on the estimation of the surface tension of fatty acid methyl esters (FAMEs) and biodiesel, including their dependence on temperature. Also, various prediction models are tested to observe their favorable and unfavorable qualities by means of statistical analysis, which also gives us the possibility to identify the best predictive model.

2. Methodologies for predicting the surface tension

Four general methodologies were considered in this work to predict the surface tension. First, the contribution group method based on the parachor, using two structural contribution groups proposed by Sugden and Knotts. Second, the corresponding state methodology, using the critical properties reported by García et al. [3]. Third, the hybrid model proposed by Goldhammer is a combination between the contribution group and corresponding state methods, and it is described in detail by Poling et al. [7]. And finally, the empirical correlations developed in this work, where the surface tension of various methyl esters was correlated with molecular weight and temperature. Fig. 1 shows a summary. It is important to emphasize that only those models that could be able to incorporate the functionality with temperature were included in this work.

On the other hand, two mixing rules were tested to estimate the surface tension of biodiesel: the Dalton mass-average method and the Kay's mixing rule.

2.1. Models for predicting the surface tension of FAMEs

In this section, the models that were tested to predict the surface tension of FAMEs are described in detail.

2.1.1. Parachor model

In 1923, Macleod proposed a correlation to estimate the surface tension of a substance from its liquid and vapor density, shortly afterwards (in 1924), the temperature-independent parameter in the Macleod's correlation was called parachor [P] by Sugden, who gives the way of how can be estimated from the structure of molecules [7]. Appendix A shows how the parachor of fifteen methyl esters was calculated using two structural contribution groups reported in the literature [8,9]. In the case of the Macleod–Sugden correlation, the temperature functionality is given through the liquid density, which must be provided at the same temperature at which the surface tension is required.

Recently, the parachor model was used by Freitas et al. [1] in order to predict the surface tension of biodiesel. However, these authors performed their calculations subject to the prior knowledge of the experimental density of methyl esters at a given temperature. Now, we are proposing to combine the parachor model [7] with the empirical correlation that was derived in the previous work [2] in order to dispense with the experimental data of density of methyl esters as follows:

$$\sigma = [P]^4 \left(\frac{1.069 + 0.0113N - 7.41 \times 10^{-4}T}{M} + \frac{3.575}{M^2} \right)^4 \quad (1)$$

where σ is the surface tension in mN/m , $[P]$ is the parachor, M is the molecular weight in g/mol , N is the number of double bonds in the fatty acid chain, and T is the temperature in K .

2.1.2. Corresponding state models

The law of corresponding states expresses the generalization that equilibrium properties that depend on certain intermolecular forces are related to the critical properties in a universal way [7]. Critical pressure (P_c), critical temperature (T_c), acentric factor (ω), and normal boiling point (T_{nb}), are used as inputs of corresponding state models to estimate the surface tension. According to our knowledge, there is little experimental information related to the critical properties of FAMEs. In this paper, these properties were estimated by using the methods reported by García et al. [3], that

Table 1
Corresponding state models.

Model	Equation
Brock and Bird	$\sigma = \left(\frac{P_c}{100} \right)^{2/3} T_c^{1/3} \left[0.1196 \left[1 + \frac{T_{br} \ln \left(\frac{P_c}{100 \cdot 2490} \right)}{1 - T_{br}} \right] - 0.279 \right] (1 - T_r)^{11/9}$
Pitzer	$\sigma = \left(\frac{P_c}{100} \right)^{2/3} T_c^{1/3} \left(\frac{1.86 + 1.18\omega}{19.05} \right) \left(\frac{3.75 + 0.91\omega}{0.291 - 0.08\omega} \right)^{2/3} (1 - T_r)^{11/9}$
Zuo and Stenby	$\sigma = \left(\frac{P_c}{100} \right)^{2/3} T_c^{1/3} \left\{ -1 + \exp \left[\ln \left(1 + \frac{40.52(1 - T_r)^{1.287}}{(190.56)^{1/3} (4599)^{2/3}} \right) \right] \left(\frac{w - 0.011}{0.399 - 0.011} \right) \left(\ln \left(1 + \frac{52.095(1 - T_r)^{1.21548}}{(568.7)^{1/3} (2490)^{2/3}} \right) - \ln \left(1 + \frac{40.52(1 - T_r)^{1.287}}{(190.56)^{1/3} (4599)^{2/3}} \right) \right) \right\}$
Sastri and Rao	$\sigma = 0.158 \left(\frac{P_c}{100} \right)^{0.5} T_b^{-1.5} T_c^{1.85} \left[\frac{1 - T_r}{1 - T_{br}} \right]^{11/9}$

where σ is the surface tension, w is the acentric factor, P_c is the critical pressure in kPa , T_c is the critical temperature in K , T_r is the reduced temperature $T_r = T/T_c$, whereas T_{br} is the reduced temperature evaluated at boiling point ($T_{br} = T_b/T_c$).

In the case of the Zuo and Stenby model, the values of 0.011, 190.56 and 4599 corresponds to the acentric factor, critical temperature in K , and critical pressure in kPa of methane (reference fluid-one); whereas 0.399, 568.7 and 2490 are the corresponding thermodynamic parameters for the n-octane (reference fluid-two).

they were grouped in the following packages: Constantinou–Gani and Wilson–Jasperson (package 1), Marrero–Pardillo and Wilson–Jasperson (package 2), Ambrose–Joback (package 3).

Once we had estimates for the critical properties of FAMEs, we estimate the surface tension of these compounds using four corresponding state models: (1) Brock and Bird, (2) Pitzer, (3) Zuo and Stenby, and (4) Sastri and Rao [7]. Table 1 presents the equations of these models with their parameters and units. Although the critical pressure was expressed in units of “bar” on the original corresponding state equations, we rearrange them to handle the critical pressure in “kPa”, according to the International System of Units (SI).

2.1.3. Combined model

Goldhammer proposed in 1910 a technique to relate the surface tension with temperature and density (by combining the contribution group and the law of corresponding states), which gives good results for various organic compounds [7]. Now, we decided to test the equation proposed by Goldhammer to estimate the surface tension of FAMEs. Again, the empirical density correlation derived in the previous work [2] was used in the Goldhammer equation to avoid the use of experimental density data of FAMEs as follows:

$$\sigma = [P]^4 \left(\frac{1.069 + 0.0113N - 7.41 \times 10^{-4}T_b}{M} + \frac{3.575}{M^2} \right)^4 \left(\frac{1 - T_r}{1 - T_{br}} \right) \quad (2)$$

where σ is the surface tension in mN/m, $[P]$ is the parachor, M is the molecular weight in g/mol, N is the number of double bonds in the fatty acid chain, and T_b is the temperature at the normal boiling point in K, T_r is the reduced temperature which is defined as the actual fluid temperature divided by its critical temperature ($T_r = T/T_c$), whereas T_{br} is the reduced boiling point temperature ($T_{br} = T_b/T_c$).

The liquid density at the normal boiling point of the Goldhammer technique is estimated from the $(1.069 + 0.0113N - 7.41 \times 10^{-4}T_b)/(M) + (3.575/M^2)$ terms. On the other hand, the temperature functionality is established by means of the reduced temperature (T_r).

2.1.4. Empirical correlations

Various empirical correlations were derived in this work to predict the surface tension of FAMEs. In order to obtain these correlations we compiled reliable experimental information in a database (see Table 2), looking for a wide range of temperature and molecular weight.

Empirical correlations were adjusted from the information of Table 2 using the least square method. Table 3 shows the parameters that were fixed for each equation, including their correlation coefficient (R^2) and standard deviation (SD). Table 3 also summarizes the source of the experimental data, the number of experimental points, and the temperature range at which the empirical correlations are valid. The correlation coefficients reported in Table 3 were in the 0.9675 to 0.9999 range, indicating that there is a linear relationship between the surface tension and temperature, at least in the range of temperature analyzed.

In order to obtain a generalized model that allows predict the surface tension of any FAME, unlike the individual correlations reported in Table 3, we developed four empirical correlations for predicting the surface tension of methyl esters, which besides temperature also include the functionality on molecular weight. The methodology was similar to that proposed in a previous work to predict the density and viscosity of methyl esters [2]. Temperature (T) and molecular weight (M) were selected as independent variables, while the surface tension (σ) as the dependant variable. The results show that the surface tension of FAMEs decreases with temperature (Table 2) and increases with its molecular weight (Fig. 2).

The influence of the number of double bonds (since, as it is well known, several unsaturated FAMEs as C16:1, C18:1, C18:2, C18:3,

C20:1, and C22:1 are commonly present in the biodiesel) was not included on the empirical correlations developed in this work, because we did not find extensive experimental information on the surface tension of these compounds, and according to our knowledge, Allen et al. [4] and Ejim et al. [5] have just reported some values for the following FAMEs: C18:1, C18:2, C18:3 and C22:1, at 313.15 K [4] and 353.15 K [5].

Then, the empirical correlations derived in this work are the following:

$$\sigma = 50.48 - 0.0986 T + 0.0353 M \quad (3)$$

where σ is the surface tension in mN/m, M is the molecular weight in g/mol, and T is the temperature in K.

If temperature and natural logarithm of molecular weight are used as independent variables, the surface tension of FAMEs can be estimated by Eq. (4).

$$\sigma = 23.71 - 0.0977 T + 6.39 \ln M \quad (4)$$

If cross-effects between variables are considered, Eqs. (5) and (6) can be applied.

$$\sigma = 54.09 - 0.1099 T + 0.0142 M + 6.563 \times 10^{-5} T \cdot M \quad (5)$$

$$\sigma = 57.27 - 0.2025 T - 0.2046 \ln M + 0.0206 T \ln M \quad (6)$$

One hundred thirty-one experimental points were used to derive the above empirical correlations. The Design-Expert software was used to adjust the parameters through the two-level-factorial method. Table 4 reports the low and high levels of each variable. The values of “4.63” and “5.7” in Table 4 correspond to the natural logarithm of methyl esters with lower and higher molecular weight.

Table 5 presents the analysis of variance (ANOVA) for the models studied in this work. Based on a confidence level of 95%, these empirical correlations were significant, because the F -value (which is the ratio of the variance due to effect and the variance due to error) was 1690.5, 1148.01, 4212.55, and 3495.66, respectively, which are much higher than the theoretical $F_{0.05}$ of 3 and 2.6, the first at two degrees of freedom (DF), and the second one reported at three degrees of freedom. On the other hand, the p -value (probability of seeing the observed F -value if the null hypothesis is true) was lesser than 0.05, which indicate that the terms of these correlations are significant. Thus, it was found that the proposed empirical models are adequate for predicting the surface tension of FAMEs within the range of temperature and molecular weight studied.

Appendix B gives some examples to illustrate how the above models can be used to predict the surface tension of methyl esters.

2.2. Models for predicting the surface tension of biodiesel

This section presents the mixing rules that were used in this work to predict the surface tension of biodiesel.

2.2.1. Dalton mass-average method

The Dalton mass-average method for predicting the surface tension of biodiesel, Eq. (7), was tested and validated by Allen et al. [4] and Shu et al. [19].

$$\sigma_b = \sum_{i=1}^n w_i \sigma_i \quad (7)$$

where w_i represents the mass fraction of the i th FAME

We decided to take advantage of the parachor method previously described by Eq. (1), and use it inside the mixing rule

Table 2

Surface tension of saturated methyl esters (experimental data bank).

Fatty acid	Methyl ester name	T (K)	$\sigma_{\text{exp}} (\text{mN/m})$
C4:0	Methyl butyrate	283.15	25.34 [10]
		283.15	25.63 [10]
		283.15	25.5 [10]
		283.15	25.34 [10]
		290.65	25.53 [11]
		293.15	25.19 [12]
		300.45	24.24 [11]
		307.95	22.61 [10]
		313.85	22.88 [11]
		319.35	21.5 [10]
		319.35	21.4 [10]
		319.35	21.39 [10]
		333.05	19.93 [10]
		334.05	20.5 [11]
		351.35	18.15 [10]
		351.35	18.05 [10]
		351.35	17.98 [10]
		360.45	17.48 [11]
C5:0	Methyl pentanoate	292.45	25.85 [11]
		293.15	25.76 [12]
		299.35	25.11 [11]
		313.95	23.58 [11]
		333.15	21.57 [11]
		359.75	18.82 [11]
C6:0	Methyl hexanoate	287.65	26.99 [11]
		291.25	26.55 [11]
		293.15	26.38 [12]
		293.15	26.37 [13]
		295.15	26.16 [13]
		297.15	25.94 [13]
		297.25	26.05 [11]
		299.15	25.75 [13]
		301.15	25.56 [13]
		303.15	25.35 [13]
		305.15	25.14 [13]
		313.15	24.2 [14]
		314.05	24.15 [11]
		333.15	22.5 [14]
		334.75	21.83 [11]
		348.15	21 [15]
		353.15	20.7 [14]
		360.05	19.52 [11]
C7:0	Methyl heptanoate	289.95	27.19 [11]
		293.15	26.98 [12]
		298.15	26.62 [11]
		315.35	24.75 [11]
		334.95	22.82 [11]
		360.35	20.35 [11]
C8:0	Methyl caprylate	284.75	28.78 [11]
		290.05	28.26 [11]
		293.15	27.93 [12]
		293.15	27.38 [13]
		295.15	27.19 [13]
		297.05	27.64 [11]
		297.15	26.97 [13]
		299.15	26.75 [13]
		301.15	26.57 [13]
		303.15	26.4 [13]
		305.15	26.21 [13]
		313.15	25.2 [14]
		313.15	25.4 [4]
		313.15	25.2 [16]
		313.75	25.7 [11]
		333.15	23.6 [14]
		334.45	23.84 [11]
		348.15	22.1 [15]
		353.15	21.8 [14]
		353.15	21.77 [5]
		360.55	21.16 [11]
C10:0	Methyl caprate	293.15	28.51 [12]
		293.15	28.47 [13]

Table 2 (continued)

Fatty acid	Methyl ester name	T (K)	$\sigma_{\text{exp}} (\text{mN/m})$
C12:0	Methyl laurate	295.15	28.33 [11]
		297.15	28.09 [13]
		301.15	27.69 [13]
		305.15	27.32 [13]
		313.15	26.1 [14]
		313.15	26.3 [4]
		313.15	26.1 [16]
		314.55	26.51 [11]
		333.15	24.6 [14]
		335.45	24.7 [11]
		348.15	23.3 [15]
		353.15	22.8 [14]
		353.15	22.83 [5]
		361.25	22.27 [11]
		286.55	30.22 [11]
		291.35	29.7 [11]
		293.15	28.3 [17]
		295.45	29.36 [11]
		313.15	27 [14]
		313.15	27.2 [4]
C14:0	Methyl myristate	313.15	27 [16]
		314.95	27.68 [11]
		333.15	25.4 [14]
		335.45	25.77 [11]
		348.15	24.3 [15]
		353.15	23.8 [14]
		353.15	23.61 [5]
		360.05	23.64 [11]
		293.15	30.16 [13]
		295.15	29.97 [13]
		297.15	29.75 [13]
		299.15	29.56 [13]
		301.15	29.38 [13]
		303.15	29.22 [13]
		305.15	29.06 [13]
		313.15	27.8 [14]
		313.15	27.9 [4]
		313.15	27.8 [16]
		333.15	26 [14]
C15:0	Methyl pentadecanoate	348.15	25 [15]
		353.15	24.6 [14]
		353.15	24.19 [5]
		299.15	29.41 [18]
		308.15	28.38 [18]
		323.65	27.35 [18]
		338.15	26.11 [18]
		313.15	28.4 [14]
		313.15	28.4 [4]
		313.15	28.4 [16]
		333.15	26.8 [14]
		348.15	25.7 [15]
		353.15	25.3 [14]
		353.15	25.2 [5]
		313.15	29.1 [14]
		313.15	29 [4]
		313.15	29.1 [16]
		333.15	27.5 [14]
		348.15	26.1 [15]
		353.15	26 [14]
		353.15	25.82 [5]
C16:0	Methyl palmitate	313.15	28.4 [14]
		313.15	28.4 [4]
C18:0	Methyl stearate	313.15	29.1 [14]
		313.15	29 [4]
		313.15	29.1 [16]
		333.15	27.5 [14]
		348.15	26.1 [15]
		353.15	26 [14]
		353.15	25.82 [5]

described by Eq. (7), which gives the following result:

$$\sigma_b = \sum_{i=1}^n w_i \left([P_i]^4 \left(\frac{1.069 + 0.0113N_i - 7.41 \times 10^{-4}T}{M_i} + \frac{3.575}{M_i^2} \right)^4 \right) \quad (8)$$

2.2.2. Kay's mixing rule

The Kay's mixing rule can be used for biodiesel because it is a mixture of methyl esters where deviations from ideal solution

behavior are not large (the excess surface tension is very small) [2]. The Kay's mixing rule is expressed for biodiesel by the sum of the surface tension of each FAME multiplied by its mole fraction, Eq. (9).

$$\sigma_b = \sum_{i=1}^n x_i \sigma_i \quad (9)$$

where σ_b and σ_i are the surface tension of biodiesel and i th FAME (in mN/m), whereas x_i represents the mole fraction of the i th FAME.

In a similar way as was done previously, the substitution of Eq. (1) into Eq. (9) gives the following expression:

$$\sigma_b = \sum_{i=1}^n x_i \left([P_i]^4 \left(\frac{1.069 + 0.0113N_i - 7.41 \times 10^{-4}T}{M_i} + \frac{3.575}{M_i^2} \right)^4 \right) \quad (10)$$

in which $[P_i]$ is the parachor of the i th FAME, M_i is the molecular weight of the i th FAME in g/mol, N is the number of double bonds into the fatty acid chain of the i th FAME, and T is the temperature in K.

The appendix B gives some examples to illustrate how the above models can be used to predict the surface tension of biodiesel.

3. Results and discussion

In this section, the results obtained by the models are presented. First, the models for the surface tension of FAMEs and,

second the corresponding ones for biodiesel. We also discuss their predictive capability by means of statistical analysis.

3.1. Estimation of the surface tension of methyl esters

The capability of models for predicting the surface tension of methyl esters was verified by the standard deviation (SD), correlation coefficient (R^2) and average absolute deviation ($AAD = |D|/n_{exp}$), as can be seen in Table 6.

The AADs obtained by the parachor model were 4.82%, 1.32% and 1.33% (methodologies I, II, and III, respectively). The structural contribution groups suggested by Sugden to estimate the parachor of methyl esters were used in the methodology I; whereas the corresponding suggested by Knotts were used in the methodologies II and III. Methodologies II and III differ in the training set (TS). 8697 experimental points were used by Knotts in the first TS, where an uncertainty less than 5% was obtained; whereas in the second TS, 6073 experimental points were used, and an uncertainty less than 1% was obtained by Knotts [9]. Some examples of these methodologies are reported in appendix A.

Deviations for the corresponding state models (methodologies IV to XV) were in the range of 4.64–29.72%. The Pitzer model was superior to the Brock-Bird, Sastri-Rao, and Zuo-Stenby in the prediction of the surface tension of FAMEs. Additionally, the predictions were better when the Ambrose-Joback method (package 3) was used instead of the Constantinou-Gani and

Table 3
Empirical correlations derived in this work for individual fatty acid methyl esters (FAMEs).

Reference	Fatty acid	Methyl ester name	Methyl ester formula	M (g/mol)	n_{exp}	Temperature range (K)	Empirical Correlation	R^2	SD
[10,12]	C4:0	Methyl butyrate	$C_5H_{10}O_2$	102.1317	18	[283.15, 360.45]	$\sigma = 56.73 - 0.1098 T$	0.984	0.37
[11,12]	C5:0	Methyl pentanoate	$C_6H_{12}O_2$	116.1583	6	[292.45, 359.75]	$\sigma = 56.37 - 0.1044 T$	0.9999	0.01
[11–15]	C6:0	Methyl hexanoate	$C_7H_{14}O_2$	130.1849	18	[287.65, 360.05]	$\sigma = 55.58 - 0.0997 T$	0.9959	0.15
[11,12]	C7:0	Methyl heptanoate	$C_8H_{16}O_2$	144.2114	6	[289.95, 360.35]	$\sigma = 55.92 - 0.0987 T$	0.9992	0.09
[4,5,11–16]	C8:0	Methyl caprylate	$C_9H_{18}O_2$	158.2380	21	[284.75, 360.55]	$\sigma = 56.14 - 0.0975 T$	0.986	0.28
[4,5,11–16]	C10:0	Methyl caprate	$C_{11}H_{22}O_2$	186.2912	16	[293.15, 361.25]	$\sigma = 55.35 - 0.0921 T$	0.9919	0.2
[4,5,11,14–17]	C12:0	Methyl laurate	$C_{13}H_{26}O_2$	214.3443	14	[286.55, 360.05]	$\sigma = 55.12 - 0.0885 T$	0.9675	0.43
[4,5,13–16]	C14:0	Methyl myristate	$C_{15}H_{30}O_2$	242.3975	14	[293.15, 353.15]	$\sigma = 58.13 - 0.0958 T$	0.9902	0.22
[18]	C15:0	Methyl pentadecanoate	$C_{16}H_{32}O_2$	256.4241	4	[299.15, 338.15]	$\sigma = 53.75 - 0.0818 T$	0.9919	0.16
[4,5,14–16]	C16:0	Methyl palmitate	$C_{17}H_{34}O_2$	270.4507	7	[313.15, 353.15]	$\sigma = 52.94 - 0.0784 T$	0.9994	0.04
[4,5,14–16]	C18:0	Methyl stearate	$C_{19}H_{38}O_2$	298.5038	7	[313.15, 353.15]	$\sigma = 54.23 - 0.0804 T$	0.9962	0.1

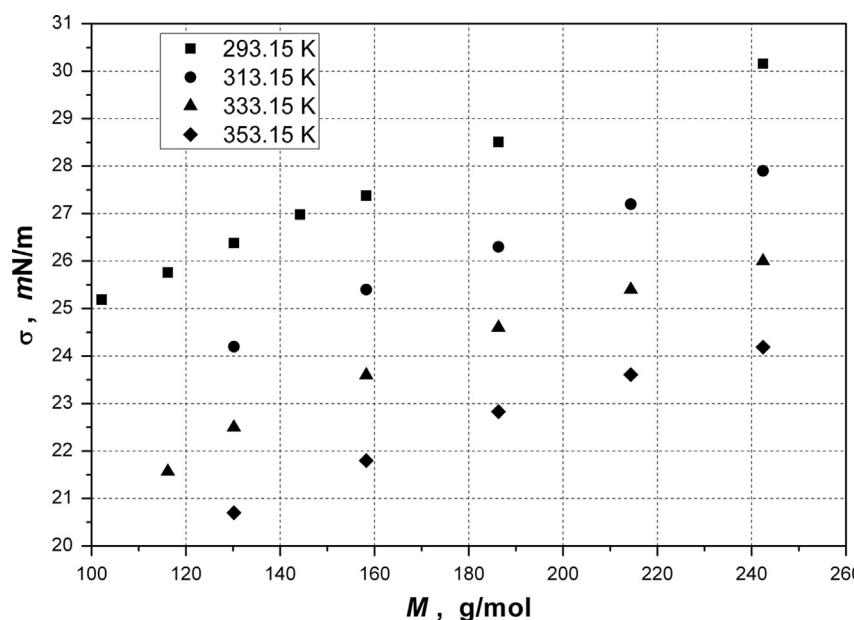


Fig. 2. Surface tension versus molecular weight of FAMEs.

Wilson–Jasperson method (package 1) or the Marrero–Pardillo and Wilson–Jasperson method (package 2).

The combined model proposed by Goldhammer was also tested in this work (methodologies XVI to XXIV). The Sugden and Knotts models were used to calculate the parachor of FAMEs, while the critical properties of methyl esters were estimated using the methods reported by García et al. [3]. In this case, the smallest deviation ($AAD=6.49\%$) was obtained when the training set with 5% of uncertainty (for estimating the structural contribution

groups) in combination with package 1 (for estimating the critical properties) were used.

The deviation obtained with the four empirical correlations is reported in Table 6. The smaller deviation ($AAD=0.93\%$) was obtained by Eq. (6), where the surface tension is a function of both temperature and natural logarithm of molecular weight, and where they are used the crossed terms.

Considering the fact of methodologies II, XXVII, and XXVIII were the ones that had the lowest: SD , R^2 , and AAD (see Table 6), we decided to include the relative error (D) of each experimental point in order to observe in detail the predictive capability of those correlations (see Fig. 3).

3.2. Estimation of the surface tension of biodiesel

As already mentioned above, it is essential to have reliable experimental data to develop predictive models. For this reason, experimental surface tension and chemical composition of biodiesel were compiled from literature. Tables 7 and 8 show the composition

Table 4
Factors and levels for full factorial design of empirical correlations.

Factor	Low level	High level
T	283.15	361.25
M	102.1317	298.5038
$\ln M$	4.63	5.7

Table 5
Analysis of variance (ANOVA).

	Sum of squares	Degrees of freedom (DF)	Mean square	F-value	p-value
Regression of Eq. (3)	1030.42	2	515.21	1690.5	< 0.0001
Residual of Eq. (3)	39.01	128	0.3		
Regression of Eq. (4)	1031.4	3	343.8	1148.01	< 0.0001
Residual of Eq. (4)	38.03	127	0.3		
Regression of Eq. (5)	1053.43	2	526.71	4212.55	< 0.0001
Residual of Eq. (5)	16	128	0.13		
Regression of Eq. (6)	1056.64	3	352.21	3495.66	< 0.0001
Residual of Eq. (6)	12.8	127	0.1		

Table 6
Standard deviation (SD), correlation coefficient (R^2), and average absolute deviations (AAD) for the surface tension of methyl esters.

Methodology	SD	R^2	AAD (%)
I. Macleod–Sugden (Sugden parameters)	0.61	0.9326	4.82
II. Macleod–Sugden (Knotts parameters, TS at 5%)	0.34	0.9764	1.32
III. Macleod–Sugden (Knotts parameters, TS at 1%)	0.36	0.9743	1.33
IV. Brock and Bird (package 1)	4.48	0.0234	17.69
V. Brock and Bird (package 2)	2.13	0.6548	11.64
VI. Brock and Bird (package 3)	0.66	0.9137	10.6
VII. Pitzer (package 1)	4.77	0.0325	29.72
VIII. Pitzer (package 2)	3.19	0.5778	10.57
IX. Pitzer (package 3)	1.42	0.7898	4.64
X. Sastri and Rao (package 1)	1.52	0.5792	10.03
XI. Sastri and Rao (package 2)	2.81	0.593	10.86
XII. Sastri and Rao (package 3)	1.41	0.7726	5.35
XIII. Zuo and Stenby (package 1)	4.4	0.0263	19.34
XIV. Zuo and Stenby (package 2)	2.34	0.6309	10.41
XV. Zuo and Stenby (package 3)	0.79	0.8853	7.57
XVI. Goldhammer (Sugden parameters, package 1)	2.27	0.1731	9.28
XVII. Goldhammer (Sugden parameters, package 2)	3.57	0.0423	11.52
XVIII. Goldhammer (Sugden parameters, package 3)	2.55	0.1479	8.49
XIX. Goldhammer (Knotts parameters, TS at 5%, package 1)	1.96	0.3007	6.49
XX. Goldhammer (Knotts parameters, TS at 5%, package 2)	3.34	0.0745	11.56
XXI. Goldhammer (Knotts parameters, TS at 5%, package 3)	2.24	0.2479	7.62
XXII. Goldhammer (Knotts parameters, TS at 1%, package 1)	1.97	0.2989	6.6
XXIII. Goldhammer (Knotts parameters, TS at 1%, package 2)	3.34	0.0742	11.44
XXIV. Goldhammer (Knotts parameters, TS at 1%, package 3)	2.24	0.2464	7.56
XXV. $\sigma = f(M, T)$ without crossed effects	0.49	0.9686	1.55
XXVI. $\sigma = f(M, T)$ with crossed effects	0.49	0.9655	1.62
XXVII. $\sigma = f(\ln M, T)$ without crossed effects	0.33	0.9834	0.95
XXVIII. $\sigma = f(\ln M, T)$ with crossed effects	0.3	0.9829	0.93

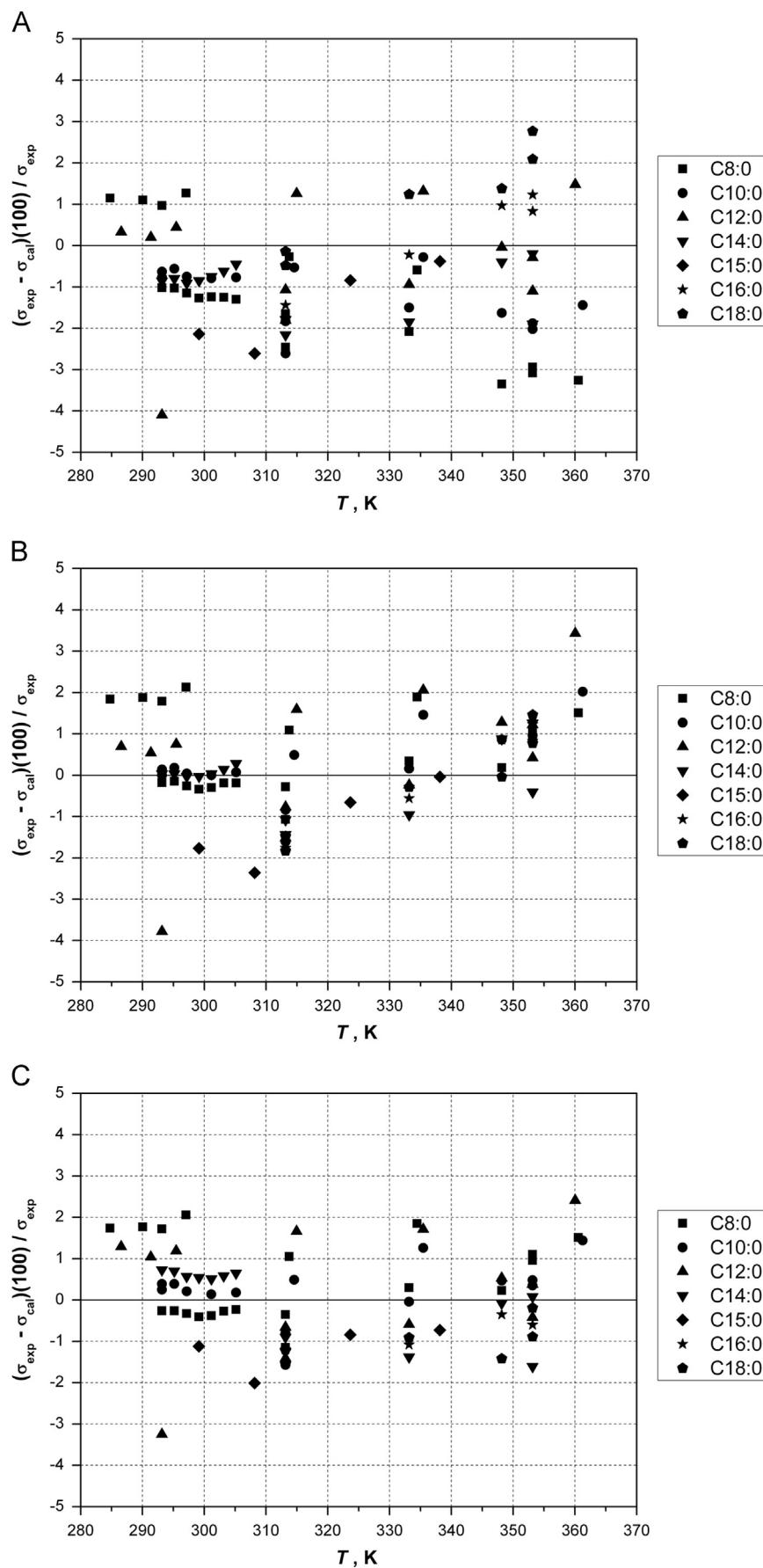


Fig. 3. Relative error: (A) Methodology II, Macleod-Sugden by using the structural contribution groups proposed by Knotts (TS with 5% of uncertainty), (B) Methodology XVII, $\sigma = f(\ln M, T)$, without crossed effects, (C) Methodology XXVIII, $\sigma = f(\ln M, T)$, with crossed effects.

Table 7Methyl ester composition, expressed in mass fraction (w_i), of biodiesel samples.

Reference	Biodiesel	w_i																			
		C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C20:3	C22:0	C22:1	C22:2	C22:3	C24:0	C24:1
[1]	Soybean A (Freitas)	–	–	–	–	0.1618	–	0.0382	0.288	0.5046	–	–	–	–	–	–	–	–	–	–	
[1]	Soybean B (Freitas)	–	–	–	0.0007	0.1076	0.0007	0.0394	0.2296	0.5353	0.0702	0.0038	0.0023	–	–	0.008	0.0024	–	–	–	
[1]	Rapeseed (Freitas)	–	0.0001	0.0004	0.0007	0.0522	0.002	0.0162	0.6211	0.2107	0.0695	0.006	0.0135	–	–	0.0035	0.0019	–	–	0.0022	
[1]	Palm (Freitas)	–	0.0003	0.0024	0.0057	0.4245	0.0013	0.0402	0.4192	0.098	0.0009	0.0036	0.0015	–	–	0.0009	–	–	–	0.0015	
[1]	A. Soybean+Rapeseed (Freitas)	–	–	0.0002	0.0013	0.1057	0.0013	0.0266	0.4105	0.3667	0.071	0.0044	0.0067	–	–	0.0045	0.0012	–	–	–	
[1]	B. Soybean+Rapeseed (Freitas)	–	–	0.0003	0.0009	0.089	0.0015	0.0276	0.4182	0.3751	0.0702	0.0046	0.0068	–	–	0.0046	0.0012	–	–	–	
[1]	Rapeseed+Palm (Freitas)	–	0.0002	0.002	0.0054	0.2309	0.0017	0.0302	0.5292	0.1547	0.0308	0.0049	0.0067	–	–	0.0024	0.0009	–	–	–	
[1]	Soybean+Palm (Freitas)	–	0.0001	0.0018	0.0001	0.2556	0.0011	0.0404	0.3313	0.3172	0.0358	0.0039	0.002	–	–	0.0032	0.0012	–	–	0.0063	
[1]	Soybean+Rapeseed+Palm (Freitas)	–	0.0001	0.0014	0.0038	0.1907	0.0014	0.033	0.4274	0.2808	0.0468	0.0046	0.0053	–	–	0.0033	0.0015	–	–	–	
[1]	Sunflower (Freitas)	–	–	0.0002	0.0007	0.064	0.0009	0.0422	0.239	0.6416	0.0012	0.0003	0.0015	–	–	0.0076	0.0008	–	–	–	
[4]	Coconut (Allen)	0.075	0.06	0.533	0.171	0.073	–	0.019	0.055	0.014	–	–	–	–	–	–	–	–	–	–	
[4]	Peanut (Allen)	–	–	–	–	0.105	–	0.027	0.466	0.301	0.01	–	–	–	–	–	–	–	–	–	
[4]	Soybean (Allen)	–	–	–	–	0.058	–	0.017	0.6	0.199	0.096	–	–	–	–	–	–	–	–	–	
[4]	Palm (Allen)	–	–	0.004	0.013	0.481	–	0.04	0.373	0.08	0.002	–	–	–	–	–	–	–	–	–	
[4]	Canola (Allen)	–	–	–	–	0.046	–	0.021	0.618	0.189	0.097	–	–	–	–	–	–	–	–	–	
[19]	Peanut (Shu)	–	–	–	–	0.104	–	0.089	0.471	0.329	0.005	–	–	–	–	–	0.002	–	–	–	
[19]	Canola (Shu)	–	–	–	0.001	0.039	–	0.031	0.602	0.211	0.111	–	–	–	–	–	0.005	–	–	–	
[19]	Coconut (Shu)	0.083	0.06	0.467	0.183	0.092	–	0.029	0.069	0.017	–	–	–	–	–	–	–	–	–	–	
[19]	Palm (Shu)	0.001	0.001	0.009	0.013	0.439	–	0.049	0.39	0.095	0.003	–	–	–	–	–	–	–	–	–	
[19]	Soybean (Shu)	–	–	–	0.001	0.103	–	0.047	0.225	0.541	0.083	–	–	–	–	–	–	–	–	–	
[19]	Corn (Shu)	–	–	–	–	0.099	–	0.031	0.291	0.568	0.011	–	–	–	–	–	–	–	–	–	
[19]	Safflower (Shu)	–	–	–	0.001	0.066	–	0.033	0.144	0.755	0.001	–	–	–	–	–	–	–	–	–	
[19]	Sunflower (Shu)	–	–	–	0.001	0.06	–	0.059	0.16	0.714	0.006	–	–	–	–	–	–	–	–	–	
[19]	Cottonseed (Shu)	–	–	–	–	0.008	0.229	–	0.031	0.185	0.542	0.005	–	–	–	–	–	–	–	–	
[19]	Lard (Shu)	–	0.001	0.001	0.014	0.255	–	0.158	0.471	0.089	0.011	–	–	–	–	–	–	–	–	–	
[20]	Camelina (Moser)	–	–	–	0.001	0.068	–	0.027	0.197	0.196	0.326	0.015	0.124	0.013	0.008	0.002	0.023	–	–	–	
[20]	Canola (Moser)	–	–	–	–	0.046	0.002	0.021	0.643	0.202	0.076	0.007	–	–	–	0.003	–	–	–	–	
[20]	Palm (Moser)	–	–	0.003	0.011	0.419	0.002	0.046	0.412	0.103	0.001	0.003	–	–	–	–	–	–	–	–	
[20]	Soybean (Moser)	–	–	–	–	0.105	–	0.041	0.241	0.536	0.077	–	–	–	–	–	–	–	–	–	
[21]	Field pennycress (Moser)	–	–	–	0.001	0.031	0.002	0.005	0.126	0.224	0.118	0.003	0.086	0.016	–	0.006	0.328	0.007	0.003	–	0.029
[22]	Hazelnut (Moser)	–	–	–	–	0.051	0.004	0.021	0.783	0.131	0.002	0.002	0.003	–	–	–	–	–	–	–	
[22]	Peanut (Moser)	–	–	–	–	0.067	–	0.023	0.789	0.044	–	0.012	0.019	–	–	0.026	–	–	–	0.018	
[22]	Walnut (Moser)	–	–	–	–	0.072	–	0.026	0.159	0.607	0.128	–	0.002	–	–	–	–	–	–	–	

Table 8Methyl ester composition, expressed in mol fraction (x_i), of biodiesel samples.

Reference	Biodiesel	x_i																				
		C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C20:3	C22:0	C22:1	C22:2	C22:3	C24:0	C24:1	
[1]	Soybean A (Freitas)	–	–	–	–	0.1754	–	0.0375	0.2848	0.5023	–	–	–	–	–	–	–	–	–	–	–	
[1]	Soybean B (Freitas)	–	–	–	0.0008	0.1165	0.0008	0.0386	0.2267	0.5322	0.0703	0.0034	0.0021	–	–	0.0066	0.002	–	–	–	–	
[1]	Rapeseed (Freitas)	–	0.0002	0.0006	0.0009	0.057	0.0022	0.016	0.6181	0.2111	0.0701	0.0054	0.0123	–	–	0.0029	0.0016	–	–	0.0017	–	
[1]	Palm (Freitas)	–	0.0005	0.0032	0.0067	0.4463	0.0014	0.0383	0.402	0.0946	0.0009	0.0031	0.0013	–	–	0.0007	–	–	–	0.0011	–	
[1]	A. Soybean + Rapeseed (Freitas)	–	–	0.0003	0.0016	0.1145	0.0014	0.0261	0.4056	0.3648	0.0711	0.0039	0.006	–	–	0.0037	0.001	–	–	–	–	
[1]	B. Soybean + Rapeseed (Freitas)	–	–	0.0004	0.0011	0.0966	0.0016	0.0271	0.4139	0.3738	0.0704	0.0041	0.0061	–	–	0.0038	0.001	–	–	–	–	
[1]	Rapeseed + Palm (Freitas)	–	0.0003	0.0027	0.0064	0.2471	0.0018	0.0293	0.5167	0.1521	0.0305	0.0043	0.006	–	–	0.002	0.0007	–	–	–	–	
[1]	Soybean + Palm (Freitas)	–	0.0002	0.0024	0.0001	0.2733	0.0012	0.0391	0.3232	0.3115	0.0354	0.0035	0.0018	–	–	0.0026	0.001	–	–	0.0048	–	
[1]	Soybean + Rapeseed + Palm (Freitas)	–	0.0002	0.0019	0.0046	0.2048	0.0015	0.0321	0.4187	0.277	0.0465	0.0041	0.0047	–	–	0.0027	0.0012	–	–	–	–	
[1]	Sunflower (Freitas)	–	–	0.0003	0.0008	0.0695	0.001	0.0415	0.2368	0.6402	0.0012	0.0003	0.0014	–	–	0.0063	0.0007	–	–	–	–	
[4]	Coconut (Allen)	0.1041	0.0707	0.5459	0.1549	0.0593	–	0.014	0.0407	0.0104	–	–	–	–	–	–	–	–	–	–	–	
[4]	Peanut (Allen)	–	–	–	–	0.125	–	0.0291	0.5059	0.329	0.011	–	–	–	–	–	–	–	–	–	–	
[4]	Soybean (Allen)	–	–	–	–	0.065	–	0.0173	0.6134	0.2048	0.0995	–	–	–	–	–	–	–	–	–	–	
[4]	Palm (Allen)	–	–	0.0053	0.0152	0.5051	–	0.0381	0.3573	0.0771	0.0019	–	–	–	–	–	–	–	–	–	–	
[4]	Canola (Allen)	–	–	–	–	0.0516	–	0.0213	0.632	0.1946	0.1006	–	–	–	–	–	–	–	–	–	–	
[19]	Peanut (Shu)	–	–	–	–	0.1127	–	0.0874	0.4657	0.3275	0.005	–	–	–	–	–	0.0017	–	–	–	–	
[19]	Canola (Shu)	–	–	–	0.0012	0.0425	–	0.0306	0.5984	0.2112	0.1119	–	–	–	–	–	0.0042	–	–	–	–	
[19]	Coconut (Shu)	0.1164	0.0714	0.4833	0.1675	0.0755	–	0.0216	0.0516	0.0128	–	–	–	–	–	–	–	–	–	–	–	
[19]	Palm (Shu)	0.0018	0.0015	0.0119	0.0151	0.4582	–	0.0463	0.3713	0.0911	0.0029	–	–	–	–	–	–	–	–	–	–	
[19]	Soybean (Shu)	–	–	–	0.0012	0.1113	–	0.046	0.2217	0.5368	0.0829	–	–	–	–	–	–	–	–	–	–	
[19]	Corn (Shu)	–	–	–	–	0.1071	–	0.0304	0.2872	0.5643	0.011	–	–	–	–	–	–	–	–	–	–	
[19]	Safflower (Shu)	–	–	–	0.0012	0.0715	–	0.0324	0.1424	0.7515	0.001	–	–	–	–	–	–	–	–	–	–	
[19]	Sunflower (Shu)	–	–	–	0.0012	0.0651	–	0.058	0.1583	0.7114	0.006	–	–	–	–	–	–	–	–	–	–	
[19]	Cottonseed (Shu)	–	–	–	0.0095	0.2444	–	0.03	0.1801	0.5312	0.0049	–	–	–	–	–	–	–	–	–	–	
[19]	Lard (Shu)	–	0.0015	0.0013	0.0167	0.2718	–	0.1526	0.458	0.0871	0.0108	–	–	–	–	–	–	–	–	–	–	
[20]	Camelina (Moser)	–	–	–	0.0012	0.0749	–	0.027	0.1981	0.1984	0.3323	0.0137	0.1139	0.012	0.0074	0.0017	0.0194	–	–	–	–	
[20]	Canola (Moser)	–	–	–	–	0.0501	0.0022	0.0207	0.6393	0.2022	0.0766	0.0063	–	–	–	0.0025	–	–	–	–	–	–
[20]	Palm (Moser)	–	–	0.004	0.0129	0.4399	0.0021	0.0438	0.3945	0.0993	0.001	0.0026	–	–	–	–	–	–	–	–	–	–
[20]	Soybean (Moser)	–	–	–	–	0.1135	–	0.0401	0.2375	0.5319	0.0769	–	–	–	–	–	–	–	–	–	–	–
[21]	Field pennycress (Moser)	–	–	–	0.0013	0.0369	0.0024	0.0054	0.1367	0.2448	0.1298	0.003	0.0853	0.016	–	0.0054	0.2993	0.0064	0.0028	–	0.0245	
[22]	Hazelnut (Moser)	–	–	–	–	0.0558	0.0044	0.0208	0.7809	0.1315	0.002	0.0018	0.0027	–	–	–	–	–	–	–	–	
[22]	Peanut (Moser)	–	–	–	–	0.0739	–	0.023	0.7941	0.0446	–	0.011	0.0175	–	–	0.0219	–	–	–	–	0.014	–
[22]	Walnut (Moser)	–	–	–	–	0.0784	–	0.0257	0.158	0.6072	0.1289	–	0.0018	–	–	–	–	–	–	–	–	–

Table 9Experimental surface tension of biodiesel samples ($\sigma_{b,exp}$).

Reference	Biodiesel	T, K	$\sigma_{b,exp}$ (mN/m)
[1]	Soybean A (Freitas)	303.15	30.89
		313.15	29.74
		323.15	28.66
		333.15	27.98
		343.15	26.97
		353.15	25.97
		303.15	31.71
[1]	Soybean B (Freitas)	313.15	30.56
		323.15	29.45
		333.15	28.16
		343.15	27.4
		353.15	26.68
		303.15	32.18
		313.15	31.17
[1]	Palm (Freitas)	323.15	30.14
		333.15	28.6
		343.15	27.39
		303.15	31.89
		313.15	30.55
		323.15	29.86
		333.15	28.62
[1]	A. Soybean + Rapeseed (Freitas)	343.15	27.84
		353.15	26.62
		303.15	31.57
		313.15	30.55
		323.15	29.54
		333.15	28.5
		343.15	27.59
[1]	B. Soybean + Rapeseed (Freitas)	353.15	26.57
		303.15	31.64
		313.15	30.52
		323.15	29.46
		333.15	27.9
		343.15	27.14
		353.15	26.22
[1]	Rapeseed + Palm (Freitas)	313.15	30.74
		323.15	29.7
		333.15	28.5
		343.15	27.71
		353.15	26.89
		303.15	31.27
		313.15	30.47
[1]	Soybean + Palm (Freitas)	323.15	29.7
		333.15	28.76
		343.15	27.68
		353.15	26.68
		303.15	31.53
		313.15	30.49
		323.15	29.4
[1]	Soybean + Rapeseed + Palm (Freitas)	333.15	28.56
		343.15	27.29
		353.15	26.07
		313.15	31.15
		323.15	29.39
		333.15	28.29
		343.15	27.47
[1]	Sunflower (Freitas)	353.15	26.04
		313.15	26.11
		323.15	28.79
		333.15	28.2
		343.15	28.5
		353.15	27.88
		313.15	28.79
[19]	Peanut (Shu)	313	27.88
		313	26.11
		313	28.5
		313	28.2
		313	28.37
		313	28.36
		313	28.37
[19]	Soybean (Shu)	313	28.21
		313	28.14
		313	29.5
		297.15	31
		313.15	29.5
		297.15	30.9
		313.15	29.4
[20]	Canola (Moser)	297.15	30.5
		313.15	29
		313.15	29.5
		297.15	31
		313.15	29.5
		313.15	27.9
		298.15	29.4
[22]	Hazelnut (Moser)	298.15	29.3
		313.15	28
		298.15	29.6
		313.15	28.6
		313.15	29.4
		298.15	29.3
		313.15	27.9
[22]	Peanut (Moser)	298.15	29.3
		313.15	28
		298.15	29.6
		313.15	28.6
		313.15	29.4
		298.15	29.3
		313.15	27.9
[22]	Walnut (Moser)	298.15	29.3
		313.15	28
		298.15	29.6
		313.15	28.6
		313.15	29.4
		298.15	29.3
		313.15	27.9

Table 9 (continued)

Reference	Biodiesel	T, K	$\sigma_{b,exp}$ (mN/m)
[20]	Palm (Moser)	313.15	29.4
[20]	Soybean (Moser)	297.15	30.5
[21]	Field pennycress (Moser)	313.15	29.5
[22]	Hazelnut (Moser)	297.15	31
[22]	Peanut (Moser)	313.15	29.6
[22]	Walnut (Moser)	298.15	29.3

expressed in mass fraction and mole fraction, respectively. These biodiesel samples were obtained from oils currently used as raw materials (such as soybean, palm, canola, rapeseed, and sunflower), as well as oils less frequently used (such as cottonseed and coconut). The mole fraction in Table 8 was derived from the mass fraction reported in Table 7, using for conversion the methodology reported in a previous work [2]. The numerical value of w_i and x_i in Tables 7 and 8 is similar, this is typical in samples of biodiesel that are composed by methyl esters with near molecular weight [2].

Thirty-three biodiesel samples (Table 9) were used at different temperatures (totaling eighty-eight experimental points) to test the predictive capability of Eqs. (8) and (10).

Figs. 4 and 5 show deviations between experimental and calculated surface tension for both biodiesel and biodiesel blends. Fig. 4 shows the results when the Dalton mass average model was tested; whereas the results for the Kay's mixing rule is reported in Fig. 5. It can be seen that positive deviations were observed for most of the biodiesel samples reported by Freitas et al. [1], while the deviation was negative in most of the samples reported by Allen et al. [4], Shu et al. [19] and Moser et al. [20–22].

The mass-average method Dalton (SD=1.03% and AAD=2.88%) proved to be slightly superior to the Kay's mixing rule (SD=1.07% and AAD=3.04%), as it is shown in Table 10.

4. Conclusions

The surface tension of pure methyl esters is estimated as a function of temperature by different models in this work.

The group contribution model based on the parachor is able to predict the surface tension of FAMEs with an overall average deviation of 4.82% (using the structural contribution groups proposed by Sugden) and 1.32% (using the structural contribution groups proposed by Knotts).

The prediction of the surface tension of methyl esters by the corresponding state methodology is closest to the experimental when the Ambrose and Joback method (package 3) is used for the estimation of the critical properties, because it gave the lowest AADs, 10.6% (Brock-Bird), 4.64% (Pitzer), 5.35% (Sastri-Rao), and 7.57% (Zuo-Stenby). The Pitzer method in conjunction with the package 3 shows to be superior to the others (Brock-Bird, Sastri-Rao, and Zuo-Stenby), in terms of its predictive ability for surface tension, presenting an overall average deviation of 4.64% for all methyl esters. The prediction of the surface tension by means of the group contribution models could be improved when more precise data for the critical properties of FAMEs are available.

We propose empirical correlations to estimate the surface tension of methyl esters that show the dependency between the surface tension with temperature and molecular weight. Our empirical model, $\sigma = f(\ln M, T)$ that takes account the crossed effects, has the best capability for surface tension of pure methyl esters, with

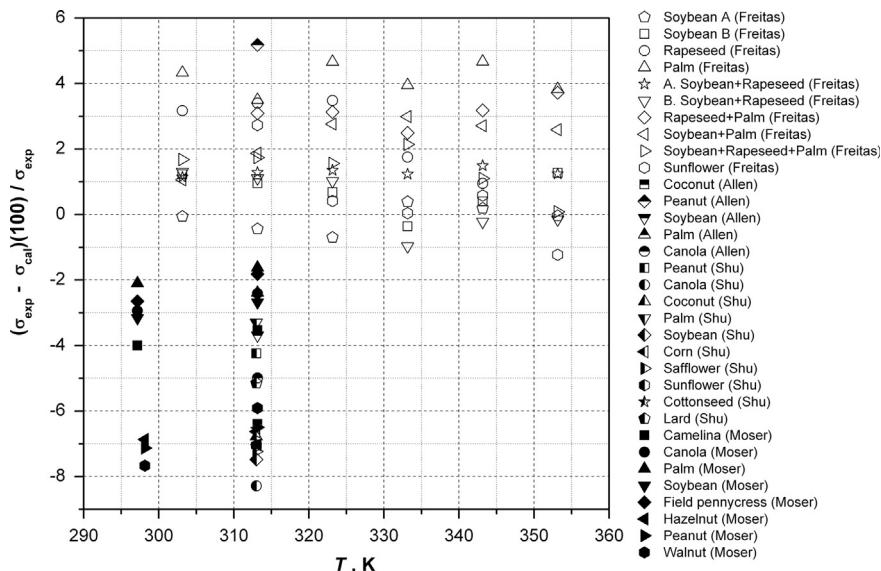


Fig. 4. Deviation pattern for the Dalton mass-average model with regard to the experimental data.

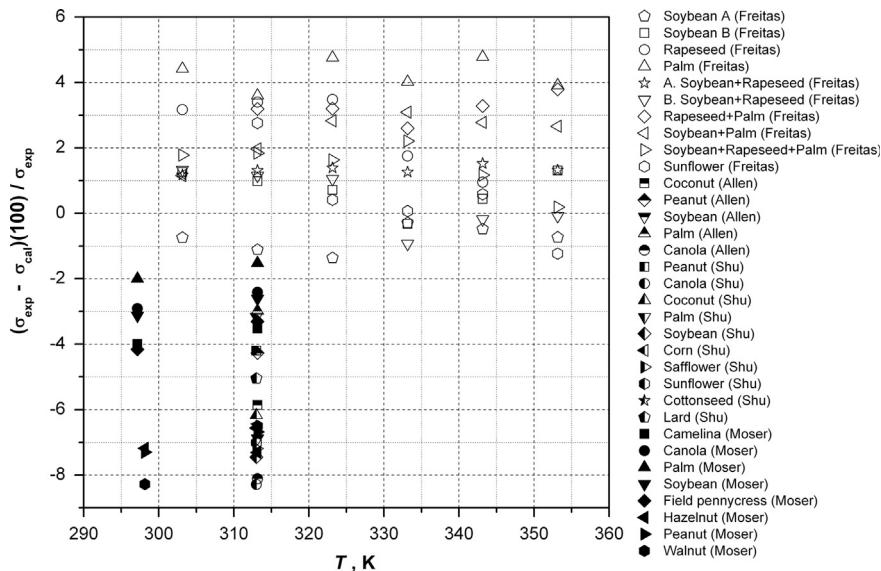


Fig. 5. Deviation pattern for the Kay's mixing rule with regard to the experimental data.

Table 10

Standard deviation (SD) and average absolute deviations (AAD) for the surface tension of biodiesel samples.

Model	SD	AAD (%)
Kay's mixing rule	1.07	3.04
Dalton mass-average method	1.03	2.88

Number of biodiesel samples=33, Number of experimental points=88

$AAD=0.93\%$. Future work may involve the improvement of empirical models through the incorporation of relationship with the number of double bonds. This will be possible when reliable experimental data on the surface tension of unsaturated FAMEs are available in the literature. It is important to note that the empirical correlations developed in this work are valid when they are applied to similar conditions (e.g. temperature) to those were used to derive them.

Two mixing rules in combination with our empirical correlations provide the advantages of estimate the density of biodiesel

without a prior knowledge of the densities of individual FAMEs. The Dalton mass-average method is superior to the Kay's mixing rule for prediction of the surface tension of biodiesel, with $AAD=2.88\%$, which is proved for 33 biodiesel samples at different temperatures (totaling 88 experimental points).

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Appendix A

This appendix shows the methodology to estimate the parachor of FAMEs by means of two structural contribution groups.

The parachor is an additive property, which would be calculated from the algebraic sum of the constituting groups of each

Table A1

Structural contribution groups proposed by Sugden [8] and Knotts [9] to estimate the parachor.

Sugden's Group	Sugden's Increment	Knotts's Group	Knotts's Increment	
			TS at 5%	TS at 1%
C (not in $-\text{CH}_2-$)	4.8	$-\text{CH}_3$	55.25	55.24
H (attached to C)	17.1	$-\text{CH}_2-$	39.92	39.9
$-\text{CH}_2-$	39	$-\text{CH}_2-$	40.11	40.11
Double bond	23.2	$-\text{CH}_2-$	40.51	40.11
$-\text{COO}-$	60	$=\text{CH}-$	34.57	34.61
		$-\text{COO}-$	64.97	64.96

compound, Eq. (A1).

$$[P] = \sum_{i=1}^n L_i S_i \quad (\text{A1})$$

where $[P]$ is the parachor, L_i is the time of occurrence of the i th structural contribution group, and S_i is the i th structural contribution group.

Table A1 reports the structural contribution of methyl ester groups [8,9]. Two training sets (TS) were considered for the structural contributions groups reported by Knott et al. The first training set was obtained by Knotts et al. from a database of 8697 experimental points with a surface tension uncertainty less than 5%, whereas for the second training set, the allowable error for 6073 data points was set at less than 1% [9]. The structural contribution of the $-\text{CH}_2-$ group, according to Knotts, increase depending of how often is repeated into the molecule.

For example, following the Sugden assignation, the parachor of methyl linolate (C18:2 FAME) can be estimated as:

$$\begin{aligned} L_1 S_1 & (7 \text{ carbon atoms, each } 4.8) = 33.6 \\ L_2 S_2 & (10 \text{ hydrogen atoms, each } 17.1) = 171 \\ L_3 S_3 & (12 \text{ }-\text{CH}_2- \text{ groups, each } 39) = 468 \\ L_4 S_4 & (2 \text{ double bonds, each } 23.2) = 46.4 \\ L_5 S_5 & (1 \text{ }-\text{COO}-, 60) = 60 \\ [P] & = 779 \end{aligned}$$

Noteworthy that only seven carbon atoms were considered for the "C" group in the methyl linolate molecule (two from the $-\text{CH}_3$, four from the $=\text{CH}-$, and one from the $-\text{COO}-$), and they must not be taken into account for the $-\text{CH}_2-$ group.

In the case of the Knotts's assignation (TS at 5% of uncertainty), the parachor of methyl linolate (C18:2 FAME) can be estimated as:

$$\begin{aligned} L_1 S_1 & (2 \text{ }-\text{CH}_3, \text{ each } 55.25) = 110.5 \\ L_2 S_2 & (12 \text{ }-\text{CH}_2- \text{ group, each } 40.11) = 481.32 \\ L_3 S_3 & (4 \text{ }=\text{CH}-, \text{ each } 34.57) = 138.28 \\ L_3 S_3 & (1 \text{ }-\text{COO}-, 64.97) = 64.97 \\ [P] & = 795 \end{aligned}$$

Double bounds must be considered carefully in the Knotts methodology. Knotts claims that a double bond is formed by using two $=\text{CH}-$ groups [9].

Tables A2 and A3 contain the structural groups of the FAMEs molecules, as well as the parachor, which were estimated according to the Sugden and Knotts methodology, respectively.

Appendix B

Some examples illustrating how models can be used to predict the surface tension of methyl esters and biodiesel samples are provided.

Example 1: Nevin et al. [14] reported that the surface tension of methyl stearate is 27.5 mN/m at 333.15 K, knowing that methyl

stearate has a molecular weight of 298.5038 g/mol. Compare with the value estimated by the models described in this work.

Solution.

a) Parachor model

The parachor is estimated as follows using the structural contribution groups of Knotts (TS at 5% of uncertainty)

$$[P] = 2(55.25) + 16(40.11) + 1(64.97) = 817$$

The surface tension is calculated by using Eq. (1) as follows:

$$\begin{aligned} \sigma & = (817)^4 \left(\frac{1.069 + 0.0113(0) - 7.41 \times 10^{-4}(333.15)}{298.5038} + \frac{3.575}{(298.5038)^2} \right)^4 = 27.16 \text{ mN/m} \\ \text{Error} & = \frac{27.5 - 27.16}{27.5} \times 100 = 1.24\% \end{aligned}$$

b) Corresponding state model

The critical properties of methyl stearate are $P_c = 1146 \text{ kPa}$, $T_c = 774.04 \text{ K}$, and $w = 1.01$ according to the Ambrose and Joback method [3]. Then $T_r = 333.15 \text{ K} / 774.04 \text{ K} = 0.4304$

By using the Pitzer model:

$$\begin{aligned} \sigma & = \left(\frac{1146}{100} \right)^{\frac{2}{3}} (774.04)^{1/3} \left(\frac{1.86 + 1.18(1.01)}{19.05} \right) \\ & \times \left(\frac{3.75 + 0.91(1.01)}{0.291 - 0.08(1.01)} \right)^{2/3} (1 - 0.4304)^{11/9} = 29.7 \text{ mN/m} \\ \text{Error} & = \frac{27.5 - 29.7}{27.5} \times 100 = -8\% \end{aligned}$$

c) Combined method

The boiling point and critical temperature of methyl stearate is 625.02 K and 774.04 K according with the Ambrose and Joback method reported by García et al. [3]. Then, $T_{br} = 625.02 \text{ K} / 774.04 \text{ K} = 0.8075$, and $T_r = 333.15 \text{ K} / 774.04 \text{ K} = 0.4304$. On the other hand the parachor is 817 as mentioned above in item (a).

The surface tension is calculated by using Eq. (2) as follows:

$$\begin{aligned} \sigma & = [817]^4 \left(\frac{1.069 + 0.0113(0) - 7.41 \times 10^{-4}(625.02)}{298.5038} + \frac{3.575}{(298.5038)^2} \right)^4 \\ & \times \left(\frac{1 - 0.4304}{1 - 0.8075} \right) = 24.19 \text{ mN/m} \\ \text{Error} & = \frac{27.5 - 24.19}{27.5} \times 100 = 12.04\% \end{aligned}$$

d) Empirical correlation

The surface tension is calculated by using Eq. (6) as follows:

$$\begin{aligned} \sigma & = 57.27 - 0.2025(333.15) - 0.2046 \ln(298.5038) \\ & + 0.0206(333.15) \ln(298.5035) = 27.75 \text{ mN/m} \end{aligned}$$

$$\text{Error} = \frac{27.5 - 27.75}{27.5} \times 100 = -0.91\%$$

Example 2. Use the Dalton mass-average method to estimate the surface tension of soybean biodiesel at 313.15 K. The experimental value is reported to be 28.2 mN/m [4].

Table A2

Parachor, [P], according to the structural contribution groups proposed by Sugden [8].

FAME	Times of occurrence					Sugden's Parachor [P]
	C (not in $-\text{CH}_2-$)	H (attached to C)	$-\text{CH}_2-$	Double bond	$-\text{COO}-$	
C8:0	3	6	6	0	1	411
C10:0	3	6	8	0	1	489
C12:0	3	6	10	0	1	567
C14:0	3	6	12	0	1	645
C16:0	3	6	14	0	1	723
C16:1	5	8	12	1	1	712
C18:0	3	6	16	0	1	801
C18:1	5	8	14	1	1	790
C18:2	7	10	12	2	1	779
C18:3	9	12	10	3	1	768
C20:0	3	6	18	0	1	879
C20:1	5	8	16	1	1	868
C22:0	3	6	20	0	1	957
C22:1	5	8	18	1	1	946
C24:0	3	6	22	0	1	1035

Table A3

Parachor, [P], according to the structural contribution groups proposed by Knotts [9].

FAME	Times of occurrence						Knotts's Parachor [P] TS at 5%	Knotts's Parachor [P] TS at 1%
	$-\text{CH}_3$	$-\text{CH}_2-\text{n}_{\text{CH}_2}=[1,11]$	$-\text{CH}_2-\text{n}_{\text{CH}_2}=[12,20]$	$-\text{CH}_2-\text{n}_{\text{CH}_2} > 20$	$=\text{CH}-$	$-\text{COO}-$		
C8:0	2	6	–	–	–	1	415	415
C10:0	2	8	–	–	–	1	495	495
C12:0	2	10	–	–	–	1	575	574
C14:0	2	–	12	–	–	1	657	657
C16:0	2	–	14	–	–	1	737	737
C16:1	2	–	12	–	2	1	726	726
C18:0	2	–	16	–	–	1	817	817
C18:1	2	–	14	–	2	1	806	806
C18:2	2	–	12	–	4	1	795	795
C18:3	2	–	10	–	6	1	784	784
C20:0	2	–	18	–	–	1	897	897
C20:1	2	–	16	–	2	1	886	886
C22:0	2	–	20	–	–	1	978	978
C22:1	2	–	18	–	2	1	967	967
C24:0	2	–	–	22	–	1	1067	1058

Solution.

The FAME composition of soybean biodiesel from Table 9 is: $w_{16:0}=0.058$, $w_{18:0}=0.017$, $w_{18:1}=0.6$, $w_{18:2}=0.199$, $w_{18:3}=0.096$. The parachor of each FAME is: $[P_{16:0}]=737$, $[P_{18:0}]=817$, $[P_{18:1}]=806$, $[P_{18:2}]=795$, $[P_{18:3}]=784$ (Table A3).

The molecular weight of each FAME is: $M_{16:0}=270.4507$ g/mol, $M_{18:0}=298.5038$ g/mol, $M_{18:1}=296.4879$ g/mol, $M_{18:2}=294.4721$ g/mol, $M_{18:3}=292.4562$ g/mol [2].

The surface tension of soybean biodiesel is calculated by the algebraic operation that sums the contributions from the molecule's parts, Eq. (8), as follows:

$$\sigma_b = (0.058) \left([737]^4 \left(\frac{1.069 + 0.0113(0) - 7.41 \times 10^{-4}(313.15)}{270.4507} + \frac{3.575}{270.4507^2} \right)^4 \right) \\ + (0.017) \left([817]^4 \left(\frac{1.069 + 0.0113(0) - 7.41 \times 10^{-4}(313.15)}{298.5038} + \frac{3.575}{298.5038^2} \right)^4 \right) \\ + (0.6) \left([806]^4 \left(\frac{1.069 + 0.0113(1) - 7.41 \times 10^{-4}(313.15)}{296.4879} + \frac{3.575}{296.4879^2} \right)^4 \right)$$

$$+ (0.199) \left([795]^4 \left(\frac{1.069 + 0.0113(2) - 7.41 \times 10^{-4}(313.15)}{294.4721} + \frac{3.575}{294.4721^2} \right)^4 \right) \\ + (0.096) \left([784]^4 \left(\frac{1.069 + 0.0113(3) - 7.41 \times 10^{-4}(313.15)}{292.4562} + \frac{3.575}{292.4562^2} \right)^4 \right)$$

$$= 29.24 \text{ mN/m}$$

$$\text{Error} = \frac{28.2 - 29.24}{28.2} \times 100 = -3.69\%$$

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